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OPTICAL RESIN COMPOSITION AND OPTICAL ELEMENT
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Specifications

1. Title of the Invention

Optical Resin Composition and Optical Element

2. Scope of Patent Claims

(1) An optical resin composition characterized by containing as the main component a copolymer comprising t-butyl styrene, a styrene and a methacrylic acid ester and/or an acrylic acid ester.

(2) An optical element that can be obtained by molding an optical resin composition characterized by containing as the main component a copolymer comprising t-butyl styrene, styrene and methacrylic acid ester and/or acrylic acid ester.

3. Detailed Description of the Invention

The present invention relates to an optical resin composition, and more specifically to an optical resin composition obtained by copolymerizing a styrene and an acrylic acid ester.

It is further related to a plastic optical element fabricated by injection molding, compression molding, or otherwise molding the above mentioned optical resin composition.

Plastic optical elements are fabricated by molding, using general purpose resins such as polystyrene, polycarbonate and acrylic resins, and the demand therefore has been increasing in recent years owing to their light weight and transparency, as well as the ease of mass producing them. However, a plastic optical element made of a conventional general purpose resin does not yield accurate imaging light paths due to the large birefringence attributable to resin characteristics and, furthermore, was not very reliable due to its instability as an optical system, with the optical element exhibiting changes in refractive index. Because of the crystallinity and molecular alignment of the resin material used, when the viscosity of a resin composition is high at the time of molding, distortion remains following cooling, and birefringence is likely to occur.

Since thermal decomposition of the resin is observed when melting and molding at a relatively high temperature to achieve satisfactory fluidity, it was important for the resin material itself to be stable. While the fluidity of a resin generally increases when the molecular weight is reduced, it results in a decrease in heat distortion temperature and, thus, deterioration of heat resistance. Therefore, there has been a demand for a resin composition

with improved fluidity, a high heat distortion temperature, and satisfactory moldability.

Improvement has been desired in particular in the case of high precision optical systems for such purposes as reading and writing information using laser beams, since it is important that the characteristics of a resin material used as an optical element include small birefringence, heat resistance, moisture resistance, and impact resistance.

Known optical resin materials that are transparent and have a relatively high refractive index include nitrated styrenes, halogenated styrenes, aminated styrenes, polycarbonates, and acrylonitrile styrene copolymer resins that are disclosed in Unexamined Patent Publication No. 56-36601. However, none is satisfactory as a resin for molding high precision optical elements, and the birefringence is large in each case.

Further, while polymethyl methacrylate has satisfactory characteristics as an optical resin with a relatively low birefringence, it has the shortfall of exhibiting profile irregularities due to changes in the environmental conditions, as well as large changes in the refractive index.

On the other hand, there also is a proposal to use such substances as a t-butyl styrene homopolymer and a t-butyl styrene - styrene copolymer (Patent Application No. 57-45133).

However, these t-butyl styrene polymers and copolymers had the shortfall of being brittle due to poor impact strength.

In view of the above mentioned situation, the object of the present invention is to provide an optical resin composition and an optical element that exhibit little heat distortion, have a high refractive index, and do not exhibit birefringence even when subjected to injection, compression, or other types of molding.

Another object of the present invention is to provide an optical resin composition with improved impact strength and satisfactory moldability.

These objects of the present invention are achieved by an optical resin composition characterized by containing as a main component a polymer comprising a t-butyl styrene, styrene and a methacrylic acid ester and/or an acrylic acid ester (hereinafter abbreviated as "(meth)acrylic acid ester") (hereinafter referred to as "copolymer of the present invention"), and an optical element obtained by molding said composition.

As a result of intense studies, the present inventors found that a copolymer comprising a t-butyl styrene, a styrene and a (meth)acrylic acid ester yields an optical resin composition exhibiting small birefringence, excelling in fluidity, and having a high heat distortion temperature, improved impact strength, and satisfactory moldability.

The preferred ratio by weight of a t-butyl styrene to the sum of a styrene and a (meth)acrylic acid ester in a copolymer of the present invention is between 1:20 to 11:9, and preferably between 1:3 and 1:10.

Further, the preferred ratio by weight of a styrene to a (meth)acrylic acid ester is from 20:1 to 1:20.

A preferred embodiment of a copolymer of the present invention contains 5 ~ 55 weight % of a t-butyl styrene with respect to total monomer units, 1 ~ 85 weight % of a styrene and 10 weight % or more of a (meth)acrylic acid ester. In a copolymer of the present invention, two or more different types of monomers may be used as the (meth)acrylic ester.

A (meth)acrylic acid ester used in a copolymer of the present invention preferably has an alkyl group having 1 ~ 10 carbon atoms.

While examples of preferred (meth)acrylic acid esters having an alkyl group include methyl acrylate, butyl

acrylate, t-butyl acrylate, methyl methacrylate, cyclohexyl methacrylate, methyl cyclohexyl methacrylate, phenyl methacrylate, isobornyl methacrylate, adamantane methacrylate glycidyl methacrylate, ethylene glycol dimethacrylate, butylene glycol methacrylate and a series of acrylic acid esters and the like used to synthesize polymers set forth in Examined Patent Publication No. 51-2519, they are not limited to these (meth)acrylic acid esters.

Examples of (meth)acrylic acid esters that are more preferable for use in a copolymer of the present invention

/3

include methyl methacrylate cyclohexyl methacrylate, and methyl cyclohexyl methacrylate phenyl methacrylate.

Next, while specific examples of copolymers of the present invention are listed below, they are not limited thereto. The figures in the parentheses show weight ratios.

(1) t-butyl styrene - styrene - methyl methacrylate

(20:40:40) MW - 200000

(2) t-butyl styrene - styrene - methyl methacrylate

(55:15:30) MW - 130000

(3) t-butyl styrene - styrene - cyclohexyl methacrylate

(15:40:45) MW - 110000

(4) t-butyl styrene - styrene - phenyl methacrylate

- (15:40:45) MW - 140000
- (5) t-butyl styrene - styrene - cyclohexyl methacrylate
- (15:40:30) MW - 160000
- (6) t-butyl styrene - styrene - methacrylic acid - 2 - methyl cyclohexyl
- (25:35:40) MW - 190000
- (7) t-butyl styrene - styrene - methyl acrylate
- (50:40:10) MW - 190000
- (8) t-butyl styrene - styrene - methyl methacrylate - cyclohexyl methacrylate
- (15:40:30:15) MW - 110000

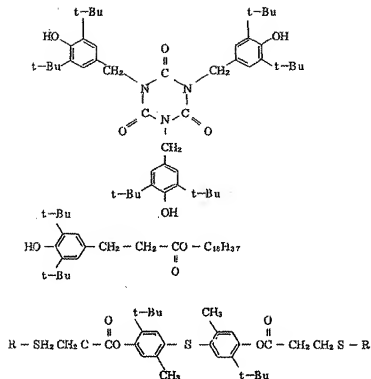
In the case of a copolymer of the present invention, to the extent that it does not significantly undermine the performances required of an optical resin, it is also possible to take such measures as the enhancement of impact resistance and dimensional precision by using various known technologies, including the interfusion of glass fibers, blending in of such rubber components as styrene - butadiene rubber, acrylic rubber and butadiene oligomers, copolymerization with acrylonitrile, and impartation of a structure similar to that of a shell-core type polymer disclosed in U.S. Patent No. 3,787,525.

The method of polymerizing a resin composition according to the present invention is not particularly limited, and

methods that may be used include suspension polymerization, emulsion polymerization, solution polymerization, bulk polymerization and radiation polymerization.

Further, a resin composition according to the present invention may contain an ultraviolet absorbing agent to enhance light resistance. Ultraviolet absorbing agents that do not go so far as to reduce visible transmittance and do not cause other resin properties to deteriorate may be used, and examples thereof include o-phenyl hydroxysalicylate compounds, o-hydroxy benzophenone compounds, 2-(o-hydroxyphenyl)-benzotriazole compounds and cyanoacrylate compounds.

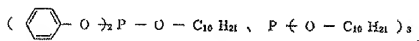
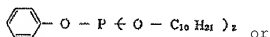
Further, it may contain a thermal stabilizer, such as 2,6-di-tert-butyl-p-cresol, 2,4-di-methyl-6-tert-butylphenol, 2,2'-methylene-bis(4-methyl-6-tert-butylphenol), 4,4'-thiobis(3-methyl-6-tert-butylphenol), 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenol) butane,



(R: an alkyl group with C₁₂ ~ C₁₄), dilauryl

/4

thiodipropionate, distearyl thiodipropionate, distearyl β,
β-thiodibutylate,



A resin composition according to the present invention may also contain a plasticizer to further enhance fluidity at the time of molding. Any substance that performs the function of a plasticizer may be used as a plasticizer, including alkyl phthalates such as 2-ethylhexyl phthalate,

n-butyl phthalate, isodecanyl phthalate, tridecanyl phthalate, heptyl phthalate and nonyl phthalate; alkyl esters of diacids such as ethylhexyl adibate, sebacic acid and 2-ethylhexyl; phosphoric acid alkyl esters such as tributyl phosphate, trioctyl phosphate, tricresyl phosphate, triphenyl phosphate and trixylenyl phosphate; epoxidized fatty acid esters such as epoxidized octyl oleate and epoxidized butyl oleate; and polyester-based plasticizers and chlorinated fatty acid esters.

Further, it can contain a lubricant such as silicon oil, dimethyl polysiloxane, aliphatic fluorocarbon, liquid or solid paraffin, butyl acid phosphate, butoxyethyl acid phosphate, 2-ethylhexyl acid phosphate, β -chloroethyl acid Phosphate, di(2-ethylhexyl) phosphate, ethylene glycol acid phosphate, (2-hydroxyethyl)methacrylate acid phosphate or an alkyl acrylate oligomer.

Methods of molding a resin composition according to the present invention to fabricate an optical element include ejection molding, compression molding, such combinations of ejection and compression molding as the Rawlinks (TN: phonetic) method and the micromolding method. Generally, all molding methods involving melting or semi-melting the resin composition may be used. Of the above mentioned molding methods, the effect of the present invention is

larger for the molding methods that resulted in relatively large birefringence when applied to the convention general-purpose resins. More specifically, the present invention may be used most favorably, for example, for the ejection method.

Birefringence, as used herein, involves the polarization of light within a propagation medium into two paths, one having ordinary wave surface and the other having extraordinary wave surface. Because light travels at different speeds as a result thereof, phase relationships are generated among the components, leading to phase differences in proportion with the medium (for example, resin) properties and sheet thickness. Phase difference ϕ is obtained by $\phi = 2\pi/\lambda (n_o - n_e)t$.

Here, n_o and n_e are the refractive indices of ordinary and extraordinary rays, t is the thickness of the medium, and λ is the wavelength in air.

Hence, the birefringence is obtained by measuring this phase difference by an optical measuring method.

With greatly improved birefringence, an optical element obtained by molding an optical resin composition according to the present invention is clearly an extremely satisfactory optical element in comparison with conventional general purpose resin.

A molded article comprising an optical resin composition according to the present invention also has improved impact resistance.

While the properties of an optical element obtained by molding a resin composition according to the present invention are improved, the surface of a molded article may be coated further in order to enhance moisture resistance even more for increased stability as a means of improving dimensional stability.

Optical elements obtained by molding a resin composition according to the present invention signify elements that function by transmitting light and include, for example, the so called lenses for still cameras, video cameras, telescopes, glasses, hard contacts and solar concentration; optical guide elements such as optical fibers and optical waveguides; and discs such as optical video and audio discs.

While the present invention is described in detail hereinafter with reference to working examples, the present

/5

invention is not limited thereto. In the following working examples, "parts" signifies parts by weight."

Working Example I

t-butyl styrene

55 parts

styrene	15 parts
methyl methacrylate	30 parts
lauroyl peroxide	0.5 parts

1 part of calcium phosphate, 0.01 part of sodium dodecyl benzene sulfonate, and 200 parts of distilled water were placed in a reactor vessel equipped with a cooling pipe, a nitrogen injection tube, a stirrer and a thermometer. The above mentioned component parts were added thereto and caused to react for 6 hours at 75° C. Upon completion of polymerization, it was treated with hydrochloric acid, rinsed with water, filtered and dried to obtain the polymer of the above mentioned specific example (2). To this polymer were added 0.2 part of 2,6-di-tert-butyl-4-methyl phenol as a thermal stabilizer and 0.1 part of a benzotriazole compound (JF-77; Johoku Chemical Co., Ltd.), and the polymer was then pelletized to obtain a resin composition. The resin composition was heated to achieve a resin temperature of 230° C and ejection molded to obtain Lens Sample 1 of the present invention, having a center thickness of 3 mm. The phase lag, which is a birefringence characteristic, was 60 degrees at the center. The refractive index was 1.54. Further, the heat distortion temperature of the present resin was 113° C according to the JISK-6871 test method.

The impact test value for the present resin was 1.6 according to the JISK-7110 Izod test method.

Working Example 2

Disc Sample 1 of the present invention having a diameter of 12.0 cm and a thickness of 1.2 mm was obtained by ejection molding the resin composition described in Working Example 1 by heating the resin to a temperature of 255° C. The phase lag, which is a birefringence characteristic, was 36 degrees.

Working Example 3

t-butyl styrene	15 parts
styrene	40 parts
cyclohexyl methacrylate	45 parts
lauroyl peroxide	1.0 parts

With the exception of using a monomer mixture comprising the above mentioned component parts, a polymer of the above mentioned concrete example (4) was obtained in the same manner as in Working Example 1. Further, the same additives as in Working Example 1 were added, and a molded lens was obtained. The center thickness of the molded lens was 3 mm and the phase lag, which is a birefringence characteristic, was 35 degrees. The refractive index was 1.51. The heat distortion temperature of the present resin was 115° C at the conditions specified for the JISK-6871 test method.

The lens shall be Lens Sample 2 of the present invention.

The impact test value for the present resin was 1.8 according to the JISK-7110 Izod test method.

Working Example 4

Disc Sample 2 of the present invention having a diameter of 12.0 cm and a thickness of 1.2 mm was obtained by ejection molding the resin composition described in Working Example 2 by heating the resin to a temperature of 260° C. The phase lag, which is a birefringence characteristic, was 15 degrees.

Working Example 5

t-butyl styrene	15 parts
styrene	40 parts
methyl methacrylate	30 parts
cyclohexyl methacrylate	15 parts
lauroyl peroxide	0.5 parts

With the exception of using a monomer mixture comprising the above mentioned component parts, a polymer of the above mentioned concrete example (8) was obtained in the same manner as in Working Example 1. Further, the same additives as in Working Example 1 were added and a molded lens was obtained. The center thickness of the molded lens was 3 mm and the phase lag, which is a birefringence characteristic,

was 40 degrees. The refractive index was

/6

1.52. The heat distortion temperature of the present resin was 116° C at the conditions specified for the JISK-6871 test method. The lens shall be Lens Sample 3 of present invention.

Working Example 6

Disc Sample 3 of the present invention having a diameter of 12.0 cm and a thickness of 1.2 mm was obtained by ejection molding the resin composition described in Working Example 3 by heating the resin to a temperature of 260° C. The phase lag, which is a birefringence characteristic, was 18 degrees.

The impact test value for the present resin was 1.7 according to the JISK-7110 Izod test method.

Comparative Example 1

Polystyrene (Styron 685; Asahi Dow Limited) was used for molding in the same manner as in Working Example 1. For a molded lens having a center thickness of 3 mm, the phase lag, which is a birefringence characteristic, was 300 degrees and the refractive index was 1.59. The heat distortion temperature of the present resin under conditions specified for the JISK-6871 test method was 87° C. The lens was used as Comparative Lens Sample 1.

The impact test value for the present resin was 1.3 according to the JISK-7110 Izod test method.

Comparative Example 2

styrene	65 parts
cyclohexyl methacrylate	35 parts
lauroyl peroxide	2 parts

With the exception of using a monomer mixture comprising the above mentioned component parts, a molded lens was obtained in the same manner as in Working Example 1. The center thickness of the molded lens was 3 mm and the phase lag, which is a birefringence characteristic, was 160 degrees. The refractive index was 1.52. The heat distortion temperature of the present resin was 92° C at the conditions specified for the JISK-6871 test method. The lens shall be Comparative Lens Sample 2.

The impact test value for the present resin was 0.9 according to the JISK-7110 Izod test method.

The samples thus obtained and the properties thereof are show in Table 1.

Table 1

サンプル No.	屈折率	位相遅れ (度)	熱変形温度 (°C)	アイゾッド衝撃試験値 Kg·cm/cm
本発明 1	1.54	60	113	1.6
2		36		
3	1.51	35	115	1.8
4		15		
5	1.52	40	116	1.7
6		18		
比較 1	1.59	300	87	1.3
2	1.52	160	92	0.9

top to bottom, left to right

Sample No.

Present Invention

Comparison

Refractive Index

Phase Lag (degrees)

Heat Distortion Temperature (° C)

Izod Impact Test Value Kg·cm/cm

As is clear from Table 1, an optical element comprising an optical resin composition according to the present invention has a relatively high refractive index, satisfactory birefringence and is resistant to heat distortion.